



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : B41M 5/00	A1	(11) International Publication Number: WO 98/05512 (43) International Publication Date: 12 February 1998 (12.02.98)
(21) International Application Number: PCT/US97/11747 (22) International Filing Date: 3 July 1997 (03.07.97) (30) Priority Data: 08/690,891 2 August 1996 (02.08.96) US (71) Applicant: MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US). (72) Inventor: WILLIAMS, Donald, J.; P.O. Box 33427, Saint Paul, MN 55133-3427 (US). (74) Agents: NEAVEILL, Darla, P. et al.; Minnesota Mining and Manufacturing Company, Office of Intellectual Property Counsel, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: INK-RECEPTIVE SHEET (57) Abstract A fast-drying ink-receptive sheet having a coating comprising a blend of from 55 % to 85 % of at least one hydrophilic liquid absorbent polymer and from 15 % to 45 % of a polyethylene-acrylic acid copolymer, having a preferred acrylic acid level of at least 10 %; such coating can be used alone, or preferably such coating is part of a coating system also including an ink-transmissive upper layer which provides improved mud-cracking properties.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon	KR	Republic of Korea	PL	Poland		
CN	China	KZ	Kazakhstan	PT	Portugal		
CU	Cuba	LC	Saint Lucia	RO	Romania		
CZ	Czech Republic	LI	Liechtenstein	RU	Russian Federation		
DE	Germany	LK	Sri Lanka	SD	Sudan		
DK	Denmark	LR	Liberia	SE	Sweden		
EE	Estonia			SG	Singapore		

INK-RECEPTIVE SHEET

Background of the Invention

The invention relates to transparent materials that can be used as ink-receptive sheets for imaging, and more particularly, to improved ink-receptive coatings thereon,
5 providing improved image quality.

Description of Related Art

Imaging devices such as ink jet printers and pen plotters are well known methods for printing various information including labels and multi-colored graphics. Presentation of such information has created a demand for transparent ink-receptive
10 imageable receptors that are used as overlays in technical drawings and as transparencies for overhead projection. Imaging with either the ink jet printer or the pen plotter involves depositing ink on the surface of these transparent receptors. These imaging devices conventionally utilize inks that can remain exposed to air for long periods of time without drying.

15 Since it is desirable that the surface of these receptors be dry and non-tacky to the touch, even after absorption of significant amounts of liquid soon after imaging, transparent materials that are capable of absorbing significant amounts of liquid while maintaining some degree of durability and transparency, are useful as imageable receptors for imaging.

20 Liquid-absorbent materials disclosed in U.S. Patent Nos. 5,134,198, 5,192,617, 5,219,928 and 5,241,006 attempt to improve drying and decrease dry time. These materials comprise crosslinked polymeric compositions capable of forming continuous matrices for liquid absorbent semi-interpenetrating polymer networks. These networks are blends of polymers wherein at least one of the polymeric components is crosslinked
25 after blending to form a continuous network throughout the bulk of the material, and through which the uncrosslinked polymeric components are intertwined in such a way as to form a macroscopically homogeneous composition. Such compositions are useful for forming durable ink absorbent, transparent graphical materials.

30 WO 8806532 (AM International) discloses a recording transparency and an aqueous method of preparation. The transparency is coated with a

hydroxyethylcellulose polymer or mixture of polymers. The coating solution may also contain a surfactant to promote leveling and adhesion to the surface, and hydrated alumina in order to impart pencil tooth to the surface.

U.S. Patent No. 5,120,601 (Asahi) discloses a recording sheet comprising an ink receiving layer containing highly water absorptive 1 to 100 μm resin particles and a binder. The resin particles protrude to a height of not less than 1 μm from the surface of the binder layer and comprise from 50 to 5,000 per 1 mm^2 surface. The resin particles include sodium, lithium and potassium polyacrylates; vinyl alcohol/acrylamide copolymer; sodium acrylate/acrylamide copolymer; cellulose polymers; starch polymers; isobutylene/maleic anhydride copolymer; vinyl alcohol/acrylic acid copolymer; polyethylene oxide modified products; dimethyl ammonium polydiallylate; and quaternary ammonium polyacrylate. Useful binders can be any hydrophilic resin, e.g., starch, gelatin, celluloses, polyethyleneimine, polyacrylamide, polyvinylpyrrolidones polyvinyl alcohols, polyester, sodium polyacrylate, polyethylene oxide, poly-2-hydroxyethyl methacrylate, crosslinked hydrophilic polymers, hydrophilic water soluble polymer complexes, and the like.

US Patent No. 4,636,805 (Canon) discloses a recording medium comprising an ink receiving layer capable of fixing an ink within 3 minutes at 20°C and 65% RH to the extent of 0.7 ml/cm^2 . One embodiment contains hydroxyethyl cellulose. Other materials are disclosed such as various gelatins; polyvinyl alcohols; starches; cellulose derivatives; polyvinylpyrrolidone, polyethyleneimine; polyvinylpyridium halide, sodium polyacrylate, SBR and NBR latexes; polyvinylformal; PMMA; polyvinylbutyral; polyacrylonitrile; polyvinylchloride; polyvinylacetate; phenolic resins and so on.

US Patent No. 4,701,837 (Canon) discloses a light transmissive recording medium having an ink receiving layer formed mainly of a water soluble polymer and a crosslinking agent. The crosslinked polymer has a crosslinking degree satisfying the water resistance of the receiving layer while giving the layer the ink receiving capacity of 0.2 ml/cm^2 . The water soluble polymer may include natural polymers or modified products thereof such as gelatin, casein, starch, gum arabic, sodium alginate, hydroxyethyl cellulose, carboxyethyl cellulose and the like; polyvinyl alcohols; complete or partially saponified products of vinylacetate and other monomers; homopolymers or copolymers with other monomers of unsaturated carboxylic acids

such as (meth)acrylic acid, maleic acid, crotonic acid and the like; copolymers or homopolymers with other vinyl monomers of sulfonated vinyl monomers such as vinylsulfonic acid, sulfonated styrene and the like; copolymers or homopolymers with other vinyl monomers of (meth)acrylamide; copolymers or homopolymers with other vinyl monomers of ethylene oxide; terminated polyurethanes having blocked isocyanate groups; polyamides having such groups as mentioned above; polyethyleneimine; polyurethane; polyester; and so on.

US Patent No. 5,277,965 (Xerox) discloses a recording medium comprising a base sheet with an ink receiving layer on one surface, and a heat absorbing layer on the other, and an anti-curl layer coated on the surface of the heat absorbing layer. The materials suitable for the ink-receptive layer can include hydrophilic materials such as binary blends of polyethylene oxide with one of the following group: hydroxypropyl methyl cellulose (Methocel), hydroxyethyl cellulose; water-soluble ethylhydroxyethyl cellulose, hydroxybutylmethyl cellulose, hydroxypropyl cellulose, methyl cellulose, hydroxyethylmethyl cellulose; vinylmethyl ether/maleic acid copolymers; acrylamide/acrylic acid copolymers; salts of carboxymethylhydroxyethyl cellulose; cellulose acetate; cellulose acetate hydrogen phthalate, hydroxypropyl methyl cellulose phthalate; cellulose sulfate; PVA; PVP; vinyl alcohol/vinylacetate copolymer and so on.

US Patent No. 5,118,570 (Xerox) discloses a transparency comprising a hydrophilic coating and a plasticizer. The plasticizer can be selected from the group consisting of anhydrides, glycerols, glycols, substituted glycerols, pyrrolidinones, alkylene carbonates, sulfolanes, and stearic acid derivatives. In one specific embodiment directed to a humidity resistant ink jet transparency, the coating comprised of a ternary mixture of hydroxypropyl cellulose, carboxymethyl cellulose, polyethylene oxide and a plasticizer. This coating can also have dispersed therein additives such as colloidal silica. Another specific is a blend comprised of polyethylene oxide and carboxymethyl cellulose together with a component selected from the group consisting of (1) hydroxypropyl cellulose; (2) vinylmethyl ether/maleic acid copolymer; (3) carboxymethyl hydroxypropyl cellulose; (4) hydroxyethyl cellulose; (5) acrylamide/acrylic acid copolymer; (6) cellulose sulfate; (7) poly(2-acrylamido-2-

methylpropane) sulfonic acid; (8) poly(vinyl alcohol); (9) poly(vinyl pyrrolidone); and (10) hydroxypropyl methyl cellulose.

U.S. Patent No. 5,068,140 (Xerox) discloses a transparency comprised of a supporting substrate and an anticurl coating or coatings thereunder. In one specific
5 embodiment, the transparency comprises of an anticurl coating comprising two layers. The ink receiving layer in one embodiment is comprised of blends of poly(ethylene oxide), mixtures of poly(ethylene oxide) with cellulose such as sodium carboxymethyl cellulose, hydroxymethyl cellulose and a component selected from the group consisting
10 of (1) vinylmethyl ether/maleic acid copolymer; (2) hydroxypropyl cellulose; (3) acrylamide/acrylic acid copolymer, (4) sodium carboxymethylhydroxyethyl cellulose; (5) hydroxyethyl cellulose; (6) water soluble ethylhydroxyethyl cellulose; (7) cellulose sulfate; (8) poly(vinyl alcohol); (9) polyvinyl pyrrolidone; (10) poly(acrylamido 2-methyl propane sulfonic acid); (11) poly(diethylenetriamine-co-adipic acid); (12) poly(imidazoline) quaternized; (13) poly(N,N-methyl-3-S
15 dimethylene piperidinium chloride; (14) poly(ethylene imine)epichlorohydrin modified; (15) poly(ethylene imine) ethoxylated; blends of poly(a-methylstyrene) with a component having a chlorinated compound.

As previously disclosed, generation of an image by an ink jet printer results in large quantities of solvent, generally blends of glycols and water, which remain in the
20 imaged areas. Hence ink-receptive coatings are coated onto substrates to absorb the solvent quickly to form good images. Many of the materials disclosed above already address this requirement for absorbency, which is magnified when substantially nonabsorbent transparent materials are used. However, even when the absorbency is adequate, diffusion of solvent into unimaged areas can result in "bleeding" of the
25 image, when the dye is carried along with the solvent.

U.S. Patent No. 5,342,688 addresses this bleeding problem. It discloses an improved ink-receptive sheet comprising a transparent substrate bearing on at least one major surface thereof an ink-receptive layer which comprises at least one hydrophilic liquid absorbent polymer and an effective amount of polymeric mordant comprising a
30 guanidine functionality.

With the advent of pigmented inks, other problems are encountered when these same prior art materials are used as ink-receptive coatings. One of the problems can

be characterized as 'mud-cracking'. Without wishing to be bound by theory, it is believed that the pigment, along with other ink components, e.g., polymeric dispersants, and possibly certain dissolved components of the receptor layer form a separate layer on the surface of the ink-receptive coating. Upon drying, this layer can
5 literally fracture, and result in cracks which are visible to the eye, and accompanying poor image quality and low optical densities. This effect is quite apparent with some printers already on the market, for example, HP Deskjet® 1200C, and is more severe with some machines than others. Therefore, other materials need to be incorporated into the coatings to improve image quality. The inventors have now discovered an ink-
10 receptive sheet useful for projecting an image, commonly called a "transparency" which, when coated with an ink-receptive coating and imaged with an ink depositing device can be successfully printed with pigmented typed-inks with good image quality.

Preferred embodiments of this invention also have reduced image bleeding, improved shelf life, even when it is exposed to elevated temperature and high humidity,
15 or in cases where solvent is prevented from leaving the coating, e.g., when stored in a transparency protector, and also display excellent drytimes.

The present invention discloses a copolymer which when added to an ink-absorbent layer, can improve the dry time of that layer while giving good image quality.

20 Summary of the Invention

Improved ink-receptive sheets of the invention have a substrate with an ink-receptive coating thereon. Ink-receptive coatings used herein comprise a hydrophilic liquid absorbent polymer, a copolymer which provides fast drying and an admixture of other additives which work together to provide a coating which will, when imaged,
25 provide a fast-drying, high-quality image with no surface cracks or bleeding.

The ink-receptive coatings used in sheets of the invention comprise a blend of from 15% to 45% by weight of a polyethylene-acrylic acid copolymer and from 55% to 85% by weight of at least one hydrophilic liquid absorbent polymer. The presence of the polyethylene-acrylic acid copolymer improves the drytime of the coating while
30 maintaining good image quality, when printed with aqueous inks. The polyethylene-

acrylic acid copolymer preferably has at least 10% by weight acrylic acid content, more preferably at least 20% by weight acrylic acid content.

In one embodiment, this invention comprises an ink-receptive coating system comprising at least two layers, a thick base layer for ink absorption comprising a polyethylene-acrylic acid copolymer and a hydrophilic liquid absorbent polymer, and a thin ink-transmissive upper layer which may function to improve tack, feeding, dry time, bleed, mud-cracking, wetting, and the like.

In a preferred embodiment of the two layer coating system, the base layer comprises a blend having from 15% to 45% by weight polyethylene-acrylic acid copolymer and from 55% to 85% of at least one hydrophilic liquid absorbent polymer, and the ink-transmissive upper layer comprises a relatively high viscosity methylcellulose or hydroxypropylmethylcellulose, or blends thereof, e.g., having a viscosity of more than 2,000 centipoise in a 20% aqueous solution. These ink-receptive coating systems have fast dry times and, when coated onto substrates, yield good image quality when printed on printers using aqueous inks including pigmented-type inks.

A highly preferred embodiment of the ink-receptive coating system have two layers, wherein the base layer comprises a polyethylene-acrylic acid copolymer and polyvinylpyrrolidone, and the ink-transmissive layer comprises

- a) a high viscosity methylcellulose binder, hydroxypropylmethylcellulose, or blends thereof, and
- b) an organic acid salt selected from the group consisting of salts of polyethyleneimine and salts of substituted polyethyleneimine.

Optional ingredients such as a mordant can also be present either in the top layer or the base or both layers.

The thickness of the single layer coating and the base layer for the two-layer coating system preferably ranges from 10 μm to 40 μm ; when used, the ink-transmissive upper layer preferably has a thickness of from 0.5 μm to 10 μm .

As used herein, these terms have the following meanings.

1. The term "mud-cracking" means a physical cracking or fracturing of the pigmented ink layer of image resulting in lower density and quality. The cracks are so called because they resemble the cracking visible in the mud of a dried river bed.

2. The terms "hydrophilic" and "hydrophilic surface" are used to describe a material that is generally receptive to water, either in the sense that its surface is wettable by water or in the sense that the bulk of the material is able to absorb significant quantities of water. Materials that exhibit surface wettability by water have hydrophilic surfaces.

3. The term "hydrophilic liquid-absorbing materials" means materials that are capable of absorbing significant quantities of water, aqueous solutions, including those materials that are water-soluble.

4. The terms "hydrophobic" and "hydrophobic surface" refer to materials which have surfaces not readily wettable by water. Monomeric units will be referred to as hydrophobic if they form water-insoluble polymers capable of absorbing only small amounts of water when polymerized by themselves.

5. The term "mordant" means a compound which, when present in a composition, interacts with a dye to prevent diffusion of dye through the composition.

6. The term "pigment layer" means that layer generated on the surface of the transparency comprised of the pigment, polymeric dispersants, and various components from the receptor layer.

7. The term "high viscosity" when used to refer to the methylcellulose compound, means having a viscosity of at least 2,000 centipoise when in a 20% aqueous solution.

All parts, percents, and ratios herein are by weight unless otherwise specifically stated.

Brief Description of the Drawing

Figure 1 show a plot wherein the abscissa shows polyethylene-acrylic acid copolymer percentage of the polymer blend in a single ink-receptive layer, plotted against the average drytime of ink-receptive sheet of the invention in minutes.

Detailed Description of the Invention

In ink jet printing, large amounts of liquid are placed onto the surface to be imaged, relative to other types of printing. The printing surface must be able to absorb all the liquid and dry quickly. If an ink-receptive sheet does not dry within minutes or even seconds, it will not meet with consumer approval. Delays in drying cause

smudging of the image, handling problems, and the inability to use the sheets immediately. Further, if stacked or stored before completely dry, they will stick to one another, or to a storage envelope.

It was particularly noticed that as the percentage of polyethylene/acrylic acid copolymer in the coating decreased to less than 50%, this effect became smaller and disappeared totally at 35%.

The ink-receptive sheets of the present invention comprise a coating system which may comprise a single relatively thick liquid-absorbent layer, or a two-layer coating system having a thick base layer and a thinner ink-transmissive upper layer. Where a single layer is used, the thickness of the single layer preferably ranges from 10 μm to 40 μm . Where a two-layer coating system is used, the base layer is the same thickness as the single layer coating, and the ink-transmissive upper layer preferably has a thickness of from 0.5 μm to 10 μm .

The absorbent layer comprises a blend of polymers to total 100%; from 15% to 45% by weight of the blend is a polyethylene-acrylic acid copolymer, correspondingly, from 55% to 85% by weight is at least one liquid-absorbent polymer. Preferred blends comprise from 20% to 35% of the polyethylene-acrylic acid copolymer. Presence of polyethylene-acrylic copolymers in the blend improves the dry time while maintaining good image quality. Preferred copolymers include those having at least 10% by weight acrylic acid content, more preferably at least 20% by weight acrylic acid content.

Also, many ink jet films smear the image as the film leaves the printer. It is particularly noticeable in imaging with lines at right angles to the direction of motion of the film through the printer. The ink moves over less-dense areas in an irregular fashion yielding smeared, unacceptable images. This effect is referred to as run/bleed.

Preferred liquid absorbent hydrophilic polymeric compounds used in the single layer system, and base layer of the two-layer system, along with the polyethylene-acrylic acid polymer include uncrosslinked hydrophilic liquid absorbent polymers such as polyacrylamides, polyvinylpyrrolidone and modified polyvinyl pyrrolidones, polyvinyl alcohol and modified polyvinyl alcohols, and other hydrophilic and liquid absorptive polymers comprising copolymerizable monomers such as:

- a) nitrogen-containing hydrophilic, and water absorptive monomers selected from the group consisting of vinyl lactams such as N-vinyl-2-

- pyrrolidone; acrylamide, methacrylamide and their N-monoalkyl and N,N-dialkyl derivatives thereof; alkyltertiaryaminoalkylacrylates and methacrylates; vinylpyridines such as 2-vinyl and 4-vinyl pyridines; preferably N-vinyl-2-pyrrolidone; acrylamide, methacrylamide and their N-monoalkyl and N,N-dialkyl derivatives thereof; and
- 5 b) hydrophilic monomers selected from the group consisting of hydroxyalkyl acrylate and methacrylate, the alkyl group having from 1 to 5 carbon atoms, preferably from 1 to 2 carbon atoms, and more preferably hydroxyethyl acrylate and methacrylate; alkoxyalkyl acrylate and methacrylate,
- 10 the alkyl group preferably ranging from 1 to 5 carbon atoms, preferably from 1 to 2 carbon atoms.

Modified polyvinylpyrrolidones include such copolymers as NVP/vinyl acetate copolymers, e.g., those available commercially from as "S-630" and "W735", NVP/DMAEMA copolymers available as Gafquat® 755, NVP/acrylic acid

15 copolymers, available as ACRYLIDONE®, and NVP/MEAHEMA/AA copolymers, such as "copolymer 958", all of which are available from I.S.P. Technologies Inc., Wayne, NJ. Modified polyvinylalcohols include polyvinylalcohols having various percentages of vinylacetate, and the like.

The preferred material for the liquid absorbent layer is a blend of

20 polyvinylpyrrolidone and polyethylene-acrylic acid. The preferred polyethylene-acrylic acids include those having at least 10%, preferably at least 20% by weight acrylic acid content. The presence of a blend of polyvinylpyrrolidone (PVP-K-90) and a polyethylene-acrylic acid copolymer having 20% acrylic acid content, Primacor® 5980, in the liquid absorbent layer gives excellent dry times, especially when used in

25 the two layer system with the preferred top layer constructions. The improved dry times are seen on essentially all ink jet printers.

The liquid absorbent layer can also comprise a crosslinked semi-interpenetrating network, or "SIPN". The SIPN for this ink-receptive coating would be formed from polymer blends comprising (a) at least one crosslinkable polyethylene-acrylic acid copolymer, (b) at least one hydrophilic liquid absorbent polymer, and (c) a

30 crosslinking agent. The SIPNs are continuous networks wherein the crosslinked

polymer forms a continuous matrix, as disclosed in U.S. Patents 5,389,723, 5,241,006, 5,376,727, and 5,208,092.

An ink-transmissive upper layer is also preferably present in addition to the liquid absorbent layer. This is applied on top of the liquid absorbent base layer. This upper layer is thinner, and comprises polymeric materials such as polyvinylpyrrolidone, polyvinyl-alcohol, modified celluloses, and mixtures thereof.

In one preferred embodiment, to maximize image quality and substantially eliminate mud-cracking with most pigmented-type inks, the upper layer contains high viscosity modified cellulose binders such as methylcellulose, hydroxypropylmethylcellulose and hydroxyethyl-methylcellulose and mixtures thereof.

In this embodiment, certain cellulose derivatives are unsuitable as binders for elimination of mud-cracking include hydroxyethyl cellulose, hydroxymethyl cellulose, and carboxymethyl cellulose, although these may be used as additives when they comprise less than 40% of the overall cellulose content, or where mud-cracking is not prevalent, or critical. Cellulose derivatives less preferred as binders due to their hydrophobic nature, water insolubility, need for organic solvents, and tendency to cause coalescence of pigmented as well as colored ink jet inks include ethylcellulose, ethylhydroxyethyl cellulose and hydroxybutyl cellulose. These may again be used as additives with appropriate solvent blends when they comprise less than 40% of the overall cellulose content. Hydroxypropyl cellulose, although water soluble, is less suitable as a binder for the same reasons as the latter materials, although it may also be used as an additive when it comprises less than 40% of the overall cellulose content.

The upper layer can also comprise organic acid salts of polyethyleneimine for further improvements in the other properties including drytime, smudging of the images, image brightness and bleeding. Useful acids include dicarboxylic acid derivatives, containing 2-14 carbon atoms, phthalic acids, hydrochloric acid, boric acid, and substituted sulfonic acids, such as methanesulfonic acid, with preferred one being p-toluenesulfonic acid. The upper layer may also comprise additives in addition to the celluloses mentioned above that can improve drytimes, color quality, tack, and the like, in greater quantities which do not degrade the mud-cracking performance of the pigmented ink. These additives include water soluble polymers such as polyacrylic acid, polyvinylpyrrolidone, GAF Copolymer 845, polyethylene oxide, water soluble

starches, e.g. Staylok® 500 and water dispersible and water suspendible clays, e.g. Laponite® RDS, and inorganic sols as long as these additives comprise less than 40% of the topcoat solids. Other additives may include colloidal silica, boric acid, and surfactants.

- 5 Another additive which may be present to control curl is a plasticizing compound, which is added to the base layer of the film. Compounds can include low molecular weight polyethylene glycols, polypropylene glycols, or polyethers; for example PEG 600 or Pycal® 94.

- 10 One preferred additive, for reduction of ink fade and bleed, is a mordant can also be present either in the top layer, the base layer, or both. If present in the top layer or base layer, the amount is preferred to range from 1 part by weight to 20 parts by weight of the solids, preferably from 3 parts by weight to 10 parts by weight.

- 15 Feedability and antiblocking properties may also be controlled by the addition of a particulate. Suitable particulates include starches, glass beads, silicas, polymeric microspheres and beads, with a preferred embodiment comprising polymethyl methacrylate (PMMA) beads. Levels of particulate are limited by the requirement that the final coating be transparent with a haze level of 15% or less, as measured according to ASTM D1003-61 (Reapproved 1979). The preferred mean particle diameter for particulate material is from 5 to 40 micrometers, with at least 25% of the particles having a diameter of 15 micrometers or more. Most preferably, at least 50% of the particulate material has a diameter of from 20 micrometers to 40 micrometers. While the particulate may be added to either or both layers, preferred embodiments contain the particulate in the upper layer.

- 20 Other optional ingredients may be present in the upper layer for the purposes of improving coatability, or other features. Useful additives include such as catalysts, thickeners, adhesion promoters, glycols, defoamers, surfactants and the like, so long as the addition does not negatively impact the drying time.

- 25 The ink-receptive layer(s), can be applied to the film backing by any conventional coating technique, e.g., deposition from a solution or dispersion of the resins in a solvent or aqueous medium, or blend thereof, by means of such processes as Meyer bar coating, knife coating, reverse roll coating, rotogravure coating, and the

like. When two layers are used, the upper layer can then be applied thereover by the same or other conventional processes.

Drying of the ink-receptive layer(s) can be effected by conventional drying techniques, e.g., by heating in a hot air oven at a temperature appropriate for the specific film backing chosen. For example, a drying temperature of about 120°C is
5 suitable for a polyester film backing.

Film substrates may be formed from any polymer capable of forming a self-supporting sheet, e.g., films of cellulose esters such as cellulose triacetate or diacetate, polystyrene, polyamides, vinyl chloride polymers and copolymers, polyolefin and
10 polyallomer polymers and copolymers, polysulphones, polycarbonates, polyesters, and blends thereof. Suitable films may be produced from polyesters obtained by condensing one or more dicarboxylic acids or their lower alkyl diesters in which the alkyl group contains up to 6 carbon atoms, e.g., terephthalic acid, isophthalic, phthalic, 2,5-,2,6-, and 2,7-naphthalene dicarboxylic acid, succinic acid, sebacic acid, adipic
15 acid, azelaic acid, with one or more glycols such as ethylene glycol, 1,3-propanediol, 1,4-butanediol, and the like.

Preferred film substrates or backings are cellulose triacetate or cellulose diacetate, poly(ethylene naphthalate), polyesters, especially poly(ethylene terephthalate), and polystyrene films. Poly(ethylene terephthalate) is most preferred.
20 It is preferred that film backings have a caliper ranging from 50 μm to 200 μm . Film backings having a caliper of less than 50 μm are difficult to handle using conventional methods for graphic materials. Film backings having calipers over 200 μm are stiffer, and present feeding difficulties in certain commercially available ink jet printers and pen
plotters.

25 When polyester film substrates are used, they can be biaxially oriented to impart molecular orientation, and may also be heat set for dimensional stability during fusion of the image to the support. These films may be produced by any conventional extrusion method.

To promote adhesion of the ink-receptive layer to the film backing, it may be
30 desirable to treat the surface of the film backing with one or more primers, in single or multiple layers. Useful primers include those known to have a swelling effect on the film backing polymer. Examples include halogenated phenols dissolved in organic

solvents. Alternatively, the surface of the film backing may be modified by treatment such as corona treatment or plasma treatment.

Image-receptive sheets of the invention are particularly suitable for the production of imaged transparencies for viewing in a transmission mode or a reflective mode, i.e., in association with an overhead projector.

The following examples are for illustrative purposes, and do not limit the scope of the invention, which is that defined by the claims.

Detailed Description of the Drawing

In Fig. 1, it is shown that when the percentage of polyethylene-acrylic acid copolymer present in the polymer blend of the ink-receptive layer is between 15% and 45%, the drytime is approximately 5 minutes or less. When the percentage either decreases below 15%, or increase 45%, the dry time increases. At highly preferred percentages of from 20% to 35%, the dry time is approximately 4 minutes or less.

Test Methods

15

Image Density

The transmissive image density is measured using Macbeth TD 903 densitometer with the gold and status A filters.

Dry Time

The environmental conditions for this test are 70°C and 50% relative humidity (RH). The print pattern consists of solid fill columns of adjacent colors. The columns are 1/4" to 1/2" wide, and 6-9 inches long. After printing the material is placed on a flat surface, then placed in contact with bond paper. A 2 kg rubber roller 2.5" wide is then twice rolled over the paper. The paper is then removed, and the dry time, D_T is calculated by using the following formula:

25

$$D_T = T_D + (L_T/L_P)T_P$$

where T_D is the length of time between the end of the printing and placing the image in contact with the bond paper. L_T is the length of image transfer to paper; L_P is the length of the printed columns, and T_P is the time of printing.

Examples

Examples 1-2 and Comparative Examples 3C-5C

These example sheets were made having a single ink-receptive layer only.

They were coated as follows:

- 5 A coating solution for the single layer was prepared containing 20 g of a 10% aqueous solution of polyvinylpyrrolidone, available as PVP-K-90 from I.S.P, 9 g of a 10% aqueous solution of polyoxyethylene aryl ether plasticizer, available as Pycal® 94 from International Chemical Industries, and 10 g of a 20% aqueous solution of polyethylene-acrylic acid copolymer in water/ammonium hydroxide, available as
- 10 Primacor® from Dow Chemical. After mixing, the mixture was coated onto a 100 µm thick polyvinylidene chloride (PVDC) primed polyethylene terephthalate (PET) film at 200 µm wet thickness and then dried at 126°C for 2.5 minutes.

Example 2 was coated in a similar way with the same level of Pycal® 94. The various polymer compositions are shown in Table 1.

15

Table 1

Example	PVP (% by wt.)	Primacor 5980 (% by wt.)	Pycal 94 per 100% polymer	PVA (% by wt.)
1	50	50	9 g	
2	65	35	9 g	
3C	100			
4C		100		
5C	50			50

These single layer ink-receptive sheets were tested in the same manner as described, and the results are reported in Table 2.

Table 2

Ex.	Dry Time (min)				
	cyan	magenta	red	blue	black
1	3.5	2.0	>13	6	>13
2	5.5	4.0	4	4	5
3C	>13	>13	>13	>13	>13
4C	>13	>13	>13	>13	>13
5C	>13	>13	>13	>13	>13

These examples show the effect of a Primacor®/PVP blend on dry time.

Example 6

- 5 This two layer example was made with a base layer similar to the single layer made in Example 1, and this layer was overcoated with an upper layer made as follows:

- 10 10 g of a 1.25% aqueous solution of Methocel®K15M was mixed with 10 g of a 1% solution of Methocel® J5MS, 0.8 g of a 28% aqueous solution of PTSA/PEI having a ratio of 1:1.8, 0.8 g of a 5% aqueous solution of boric acid, 0.2 g of a 30% aqueous solution of Ludox® LLS, and 0.5 g of a 10% aqueous solution of LokSiz® 30. The dry times were cyan 0.5 min.; magenta, 0.5 min.; red, 3.5 min.; blue, 3.5 min., and black, 8.0 minutes.

Examples 7-9

- 15 These ink-receptive sheets were 2-layer films. The base layer was made using the same formulation used in Example 2, and the top layers were as shown in Table 3.

Table 3

Ex./Upper Layer	7	8	9
Methocel® K15M	100%		
Methocel® MJ5		100%	
PVA (Vinol 540)			3.2%
LokSiz® 30			0.8%
Xanthan Gum*			2.2%
Ethanol			93.8%

*Xanthan gum was added with rapid agitation at room temperature.

These sheets were also tested as above, and the results are shown in Table 4.

- 5 Example 9 exhibited mud-cracking, which shows that when a two-layer coating system where the upper layer is made without a modified cellulose binder, mud-cracking is likely.

Table 4

Ex.	Dry Time (min)				
	cyan	magenta	red	blue	black
7	6	3	8	8	12
8	9	3.0	11	6	13
9	1.25	0.25	6.25	5.75	12

10

Examples 10-11C

These examples were 2-layer films, using the base layer formulation of Example 2 as the base layer of Example 10, while the base layer of Example 11C and both the top layers are described in Table 5.

Table 5

Base Layer				Top Layer	
Airvol 540 10%	PVP K90 10%	PEG 600 10%	P134 10%	Methocel 10%	Loksiz 30 10%
17 g	2 g	1 g	1 g	10 g	.03 g

These ink-receptive sheets were tested using the Deskjet™ 500C. The dry time and mud-cracking results are shown in Table 6.

Table 6

Examples/ Color	10	11C
	Dry Time (min.)	Dry Time (min.)
cyan	2	11
magenta	1	8
yellow	1	8
red	4	>11
green	4	>11
blue	3	>11
black	6	>11

5

Example 12

A series of ink-receptive sheets were prepared composed solely of varying ratios of polymer blends of polyvinylpyrrolidone, commercially designated PVP-K-90 from I.S.P and the 20% aqueous solution of polyethylene-acrylic acid copolymer in water/ammonium hydroxide, available as Primacor® from Dow Chemical. The sample ratios were varied in increments of 5% starting from 60% by weight polyethylene-acrylic acid/40% by weight polyvinylpyrrolidone and going to 10% by weight polyethylene-acrylic acid/90% by weight polyvinylpyrrolidone.

The samples were coated to a dry weight of 0.8g/m² from the 20% aqueous solution using a knife coater, with a gap setting of 75 micrometers. This thickness, while above that preferred for commercial use, provides similar drying characteristics to those thicknesses.

As the PVP concentration increases beyond 85%, stickiness of the sheet was noted. At 50%/50%, the drying time was 6 minutes, whereas at 30% polyethylene-acrylic acid copolymer, the drying time was 4 minutes. As the copolymer percentage increases beyond 45%, the absorptive characteristics are reduced and the ink is not

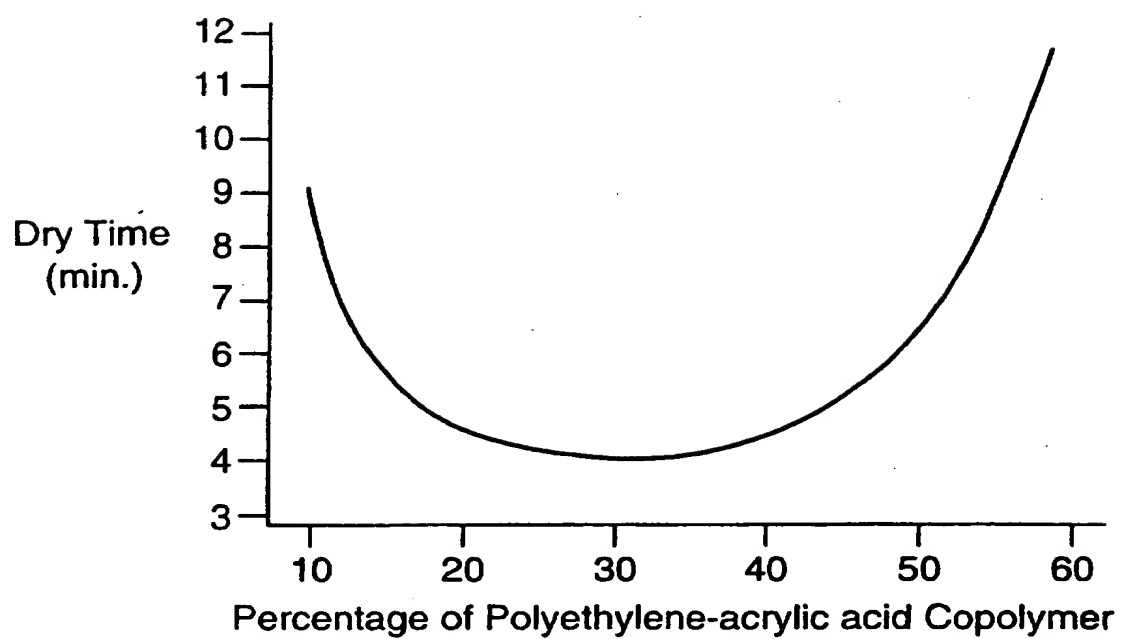
properly absorbed into the layer. This experiment was repeated and the average points plotted in Figure 1.

What is claimed is:

1. An ink-receptive sheet comprising a substrate and an ink-receptive coating, said coating comprising from 55% to 85% by weight of a hydrophilic liquid absorbent polymer selected from the group consisting of polyacrylamides,
5 polyvinylpyrrolidone, copolymers formed from N-vinyl pyrrolidone and vinyl acetate, copolymers formed from N-vinyl pyrrolidone and dimethaminoethylmetacrylate, copolymers formed from N-vinyl pyrrolidone and acrylic acid, copolymers formed from N-vinyl pyrrolidone and monoethanolaminehydroxyethylmethacrylate/acrylic acid; polyvinyl alcohol, and copolymers of polyvinyl alcohol with vinyl acetate, and
10 from 15% to 45% by weight of a polyethylene-acrylic acid copolymer wherein said polyethylene-acrylic acid copolymer comprises at least 10% by weight acrylic acid, said coating having a thickness of from 10 μm to 40 μm .
2. An ink-receptive sheet according to claim 1 wherein said polyethylene-acrylic acid copolymer comprises at least 20% by weight acrylic acid.
- 15 3. An ink-receptive sheet according to claim 1 wherein said coating comprises from 20% to 35% by weight of said polyethylene-acrylic copolymer.
4. An ink-receptive sheet comprising a coating system comprising at least two layers, a liquid absorbent base layer according to claim 1 and a thinner ink-transmissive upper layer coated thereover comprising a cellulose selected from the
20 group consisting of methylcellulose, hydroxypropyl-methylcellulose, and blends thereof, said cellulose having a viscosity of more than 2,000 centipoise as a 20% aqueous solution, said upper layer having a thickness of from 0.5 μm to 10 μm .
5. An ink-receptive sheet according to claim 4 wherein said base layer comprises from 20% to 35% by weight of said polyethylene-acrylic copolymer.
- 25 6. An ink-receptive sheet comprising a two-layer ink-receptive coating system according to claim 4, wherein said liquid absorbent base layer comprises a blend of said polyethylene-acrylic acid copolymer and polyvinylpyrrolidone.

7. An ink-receptive coating system comprising a two-layer ink receptive coating system according to claim 4 wherein said upper layer further comprises an organic acid salt selected from the group consisting of salts of polyethyleneimine and salts of substituted polyethyleneimine.
- 5 8. An ink-receptive sheet according to claim 1 wherein said coating further comprises a polymeric mordant.
9. An ink-receptive sheet according to claim 4 wherein said ink-transmissive upper layer of said two-layer ink-receptive coating system further comprises an additive to prevent mud-cracking, said additive being selected from the group consisting of water soluble starches, inorganic sols, and water dispersible clays, and a mordant.
- 10 10. An ink-receptive sheet according to claim 1 wherein said substrate is formed from a transparent polymer selected from the group consisting of cellulose triacetate, cellulose diacetate, poly(ethylene naphthalate), polyesters, and polystyrene films.
- 15 11. An ink-receptive sheet according to claim 11 wherein said polyester is poly(ethylene terephthalate).

1/1

*Fig. 1*

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 97/11747

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B41M5/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B41M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	WO 96 26840 A (MINNESOTA MINING & MFG) 6 September 1996 see page 7, line 14 - line 22 see example 2; tables 1,2 see the whole document ---	1-11
X,P	WO 96 26841 A (MINNESOTA MINING & MFG) 6 September 1996 see page 7, line 33 - page 8, line 18 see examples 5,6 see the whole document ---	4-7,9
A	EP 0 227 245 A (CANON KK) 1 July 1987 see page 5, line 50 - page 6, line 23 see page 10, line 24 - line 32 see page 15, line 36 - line 44 see the whole document --- -/--	1-11

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *S* document member of the same patent family

Date of the actual completion of the international search

15 October 1997

Date of mailing of the international search report

07.11.97

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Martins-Lopes, L

INTERNATIONAL SEARCH REPORT

Inter. nat. Application No
PCT/US 97/11747

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 889 765 A (WALLACE JOHN L) 26 December 1989 see the whole document ---	1-11
A	EP 0 583 141 A (CANON KK) 16 February 1994 see the whole document -----	1-11

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 97/11747

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9626840 A	06-09-96	NONE	
WO 9626841 A	06-09-96	US 5567507 A	22-10-96
EP 0227245 A	01-07-87	JP 1868186 C	26-08-94
		JP 62140878 A	24-06-87
		JP 1839529 C	25-04-94
		JP 62140879 A	24-06-87
		JP 1863683 C	08-08-94
		JP 62142680 A	26-06-87
		DE 3688970 D	07-10-93
		DE 3688970 T	13-01-94
		US 4785313 A	15-11-88
US 4889765 A	26-12-89	JP 2001772 A	08-01-90
EP 0583141 A	16-02-94	JP 6135124 A	17-05-94
		AT 138609 T	15-06-96
		DE 69302866 D	04-07-96
		DE 69302866 T	24-10-96
		US 5462787 A	31-10-95
		US 5565238 A	15-10-96
		JP 6136071 A	17-05-94